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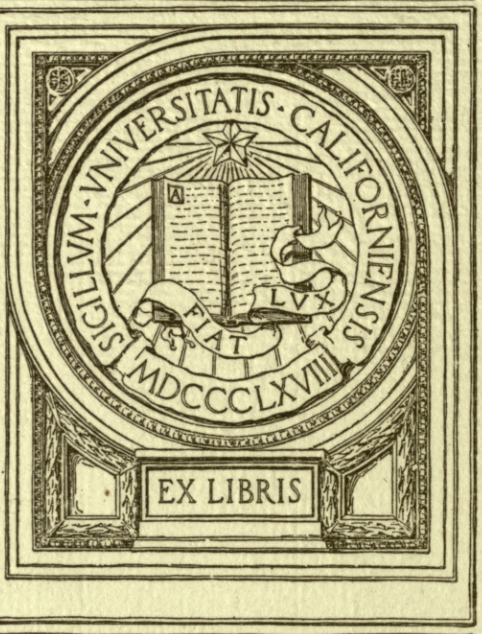

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THE ESSENTIAL OIL OF SEQUOIA SEMPERVIRENS

A thesis submitted in partial satisfaction of the requirements for the degree

of

Master of Science

at the

University of California

by

HAYWARD MERRIAM SEVERANCE

Berkeley, Cal.

April 1912

[Degree conferred, Dec. 1914. J.C.R.]

My dear Mr. Powell

The Thesis of Mr. Severance has been approved and I understand is in your possession

Edmund O'Neill

Dec. 15-1914

THE ESSENTIAL OIL OF SEQUOIA SEMPERVIRENS

No work has been done on this oil, so far as known, with the exception of that of B. R. Bowron, California '02, whose results were presented in a thesis for the bachelor's degree April 1902. So far as he was able to ascertain "no attempts have been made up to this time (1902) to investigate this oil." No mention of it has been found in the literature since that date.

The Sequoia genus comprises only two surviving species; (1) the Bigtree, Sequoia gigantea Dec. (Washingtoniana, Wellingtoniana) growing only on the western slope of the Sierra Nevada in California; (2) the Redwood, Sequoia sempervirens, growing only in a narrow belt along the Californian coast. The essential oil of the Bigtree was described by Lunge and Steinkauler in 1880 (Berichte, XIII, 1656 b, XIV 2202 b). They obtained the oil from small trees growing in Zurich, Switzerland. Their results are dis-

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cussed below. This work, quoted by Schorger and Hoffman, is the only [illegible] of the oil of the Bigtree.

The trees used in this work (Redwood) were all young growth, largely stump sprouts of 30 to 20 years, and were cut in cut over forest near Fort Bragg, Mendocino co., Cal. the last week in February 1913. A previous shipment and cutting a personal visit to the woods was lost in transit. The weather conditions here (and in general along the coast) are a temperature of about 60° and a moist atmosphere most of the time. During the two days spent at Fort Bragg a light rain fell almost continuously. This may have been partly to blame for the rapid loss of the oil from the trees after cutting and drying storage in the basement of the [illegible] building at Berkeley.

Apparatus--The oil was extracted in a steam still, shown in attached print. The still is of copper, the upper part having a perforated bottom on which the material extracted rests. The lower part contains a steam coil attached to the University heating system. Water is placed in the lower part, heated by the coil, the steam generated

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passing upward through the holes in the plate on which the material rests. In starting a run the water was also heated by a Bunsen burner until water began to come through the condenser, after which the steam coil furnished heat enough to keep a small stream of water dripping from the outlet.

The four joints of the apparatus; (1) between the top of the still and the head, (2) between the two parts of the still, (3) between head and cross piece and (4) between crosspiece and condenser, were all packed with gaskets cut from asbestos reinforced with fine wire mesh ("gas engine packing"), between brass collars tightened by brass screws. The lower side of each ring was coated with white lead and the upper with graphite. This did away with the necessity of cutting fresh rings after each run.

At the start of each run the still was filled with water to about one inch in the gauge glass. The water which distilled over was withdrawn from under the oil by a siphon and returned to the still. The oil floated on the water in the receiving bottle and was withdrawn from time to time with a pipette. In some cases a slight

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additional amount of oil separated from the milky water in the large bottle after standing overnight at the conclusion of a run and was also withdrawn. The oil was immediately transferred to a flask, kept tightly corked in the dark in a basement room.

Yield--The oil as it came over had a golden yellow color and the odor of the fresh leaves. It was nearly clear but a turbidity developed on standing.

It was impossible to make a satisfactory determination of the yield owing to several circumstances. The first of these was a delay of a week--ten days after cutting--before the still was available. The first run was interrupted by a leak in the still around the heating coil, causing another delay. The solubility of the oil in water caused a considerable loss, especially on the first run.

The first run was started March 7. Subsequent runs were made March 20, 22, 26, 27, and 29, and April 12. The rapid decline in yield showed that this was obviously and unfair test. The odor from the trees which was very pronounced at frist, declined proportionately to the yield and appeared to concentrate lower down in the branches. As the

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trees began to dry, the pleasant aromatic odor disappeared, except on breaking a twig 1-2" or more in diameter, and another quite different one took its place. There was no change in the oil except a possible slight darkening. (Owing to its being spread out in a thin layer it was impossible to determine this.

Branches were cut off the trees as needed, up to a diameter of about ½" and including all of the growth of the last year. The terpene odor was strongest in the tops of the trees, especially the new growth of the main trunk.

The still was packed tightly on the first run with 7000 grams. The other runs were made on smaller quantities up to 4600g. with the idea of hastening the time of extraction. This appeared to be complete in two to three hours in all cases except the first. When this work is resumed a quantitative determination of the yield from fresh foliage will be made.

Purification of the oil--In this way about 150cc of oil were collected (not including the oil dissolved in the water). This was rectified by distillation with steam, the oil coming over being collected fractionally in four portions of about 25cc each. The water was removed by a

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Purification of the oil--In this way about 1800c of oil were collected (not including the oil dissolved in the water). This was rectified by distillation with steam, the oil coming over being collected fractionally in four portions of about 250c each. The water was removed by a

separating funnel and the oil dried by sodium sulphate. The first fraction after being so treated was clear and colorless, with the same odor as that of the original oil but more delicate--evidently a terpene hydrocarbon. The second fraction had a light yellow green tinge, the two following a deeper color. After four fractions had been collected, the oil ceased to come over with the water and distillation was stopped.

Fractionation--The first fraction was distilled again from a 20cc flask. (There was not enough to use a Hempel column.) The oil distilled almost completely at 157--160. With about 1cc remaining the thermometer rose above 162° and the residue turned greenish yellow. The flame was removed at this point. No carbonization or decomposition was evident from the appearance or odor of the residue.

The second, third, and fourth fractions from the steam distillation were distilled again. The distillate was collected as the first fraction to 160°, the second to 165°. The temperature then rose rapidly to 190° at which most of the remainder passed over. This fraction

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Fractionation--The first fraction was distilled again from a 200c flask. (There was not enough to use a Hempel column.) The oil distilled almost completely at 157--160. With about 100 remaining the thermometer rose above 162° and the residue turned greenish yellow. The flame was removed at this point. No carbonization or decomposition was evident from the appearance or odor of the residue.

The second, third, and fourth fractions from the steam distillation were distilled again. The distillate was collected as the first fraction to 160°, the second to 165°. The temperature then rose rapidly to 190° at which most of the remainder passed over. This fraction

evidently suffered some decomposition. At 198° no more passed over and the temperature dropped. The residue (about 2cc) solidiifed on cooling. This was dissolved with ether and placed in a crystallizing dish. It failed to crystallize, remaining as a yellow wax with slight odor.

The first fraction, constituting the greater part of the oil, was distilled again and constants determined as follows;

Boiling point 157°C (Stem exposed above 54°)

Specific gravity (capillary pycnometer) $d^{15^\circ}_{15^\circ} = 0.831$

Refractive index (Abbe') $n^{18.5^\circ} = 1.473$

Polarization (Schmidt & Haensch polariscope, 10cm tube) $(a)^{D}_{20^\circ} = 24^\circ 40'$

There was no action on the oil by freshly cut sodium. The odor resembles that of the entire oil but is not so strong and each distillation appeared to diminish it slightly.

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This suggests that the odor may come from a trace of high boiling aldehyde or ester.

Ultimate analysis--0.3669g. of oil was burned in a combustion analysis, resulting as follows:

	Found	Calculated for $C_{10}H_{16}$
C	87.085	88.20
H	11.73	11.80

The low yield of carbon is apparently a result of the large quantity taken and of a slightly rapid current of oxygen and air through the tube, causing incomplete absorption of the CO_2. To drive off all moisture in the tube it was heated to the safe limit of the glass for an hour and cooled with a slow stream of purified air passing through.

Comparison with terpene from Bigtree--Lunge and Steinkauler report as their first compound form the oil of Sequoia washingtoniana a colorless oil, b. p. 155°, $d_{15°}$ 0.8522; vapor density (Victor Meyer in diphenyl amine) 69.67 ($C_{10}H_{16}$ = 68) Rotation (Wild Polaristrobometer) $(a)_j$ = 23.8

	Found		Calculated $C_{10}H_{16}$
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Addition of Bromine--Two cc of hydrocarbon were dissolved in four volumes of alcohol and four of ether, the solution cooled by ice and salt and bromine added drop by drop. Complete discoloration resulted, indicating unsaturation. Bromine was added until a yellow color appeared. On standing in ice a short time the color disappeared and a few more dops of bromine were added, shaking after each addition. When the yellow color reappeared the tube was left in ice until the ice melted but no crystals appeared. The tube was then exposed to the air. After approximately a third of the solution had evaporated a layer with a slight yellow tint appeared at the bottom. At room temperature this was slightly turbid, but cleared on warming to about 25°. After three days the solvent was driven off as much as possible by surrounding with water which was gradually brought to boiling. There still remained a volume of solvent approximately that of the oil below. The upper layer was pipetted off, some of the lower removed and placed in a clean tube, a few drops of ligroin added and the tube cooled and allowed to stand 24 hours. The oil again separated as a turbid liquid, clearing on gently warming.

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As the quantity of brominated oil on hand was not sufficient to attempt a purification by distilling, it was transferred to a boiling point apparatus and the sulphuric acid bath slowly heated. The oil gradually darkened, indicating a separation of bromine. At 50° it was red (the color of dilute ferric sulphocyanate) and at 100° almost black. At 157° fumes of bromine and hydrobromic acid came off copiously and the oil distilled into the reservoir above the air chamber. After cooling the liquid remained black, slightly more viscous and with a changed odor, but not one suggesting carbonization.

Addition of Iodine--About 1cc of oil was dissolved in an equal volume of absolute alcohol and a saturated solution of iodine in alcohol added drop by drop with shaking. No visible discoloration followed. The mixture was allowed to stand for two days and the excess alcohol was then driven off by immersing the bottle in water which was brought to a boil. The liquid which remained had a color not quite as dark as ordinary iodine tincture and a peculiar odor resembling that of anethol. Owing to lack of time work was discontinued at this point. An attempt

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to form an iodine addition compound will be made later.

Residue of the original oil--The residue which remained in the flask on the rectification by distillation with steam was separated from the water by a separating funnel and allowed to stand until the emulsion layer and presumably impurities carried over from the original distillation had settled. This left a yellow oil, thicker than the original oil as obtained from the still and with nearly the same odor. This oil was filtered through cotton, coming through perfectly clear. On heating it was found to contain a large percentage of water. Granulated calcium chloride was added and the oil allowed to stand two days with occasional shaking. A considerable amount of water separated out below the oil. An attempt was then made to distill the oil. This was a total failure under atmospheric pressure. Decomposition (and probably formation of resins) occurred before any vapor passed over. The quantity of unheated oil on hand was not sufficient for a distillation under reduced pressure and that is also deferred

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pending a new supply of foliage.

Products from the Bigtree--As the only closely allied botanical species, the Sequoia oils give an indication of possible products to expect from the redwood. Lunge and Steinkauler report the following, besides the hydrocarbon already referred to:

(2) A colorless oil turning yellow on long keeping, odor reminding of peppermint. Boiling point 227--230°, d 1.045, n about --6°

(3)In very small amount a heavy yellow oil, boiling point 280--290°.

(4) A solid body "Sequojen" with melting point 105°, boiling point 290-300°. White leaflets with weak bluish fluorescence.

This study was begun at the suggestion of Mr. Carl A. Kupfer, Forest Assistant, United States Forest Service, San Francisco, to whom I am indebted for kind assist ance at several stages of the work. Acknowledgments are also due to President Johnson and other officers of the Union Lumber Co., San Francisco, for assis-

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The work will be continued.

Chemistry Building, University of California,
Berkeley, Cal.,
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Sprout growth from Redwood stump.
Material of character used in this work.
(Photo by Forest Service.)

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